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Screening in particle attraction by capillary forces: from centimeter to nanometer scales

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Abstract—We discuss the surface-tension driven attraction of particles partially submerged in a fluid. We demonstrate a mathematical analogy between the attraction of millimeter-size particles (*Cheerios effect*) and nanometer-size particles used in directed self-assembly experiment. The Helmholtz equation for fluid/air interface is solved numerically using integral equation methods, and the force between an arbitrary number of particles can be computed. We make detailed study of the interaction of two and three particles and compare our findings with the established results from the literature. In particular, we discuss the validity of the geometric screening assumption.

1. "Cheerios effect" and its technological significance

Particles floating on water's surface usually tend to form clumps of irregular (but roughly circular) shape. This particular phenomenon is sometimes referred to as *Cheerios effect*, taking its name from the popular morning cereal. Clumping of Cheerios in a bowl may seem like an entertaining, but hardly relevant physical phenomenon. However, surprisingly enough, this effect is used on the forefront of current technological development of material science, namely, the quest for speed and miniaturization of devices. Indeed, if continuous miniaturization of microelectronic devices is to continue unabated, by 2015-2020 we will exhaust the possibilities offered by current *top-down* lithographic technologies. Thus, the *bottom-up* process of *self-assembly* has been suggested as the new technique which may take over the role of traditional technologies in the mass assembly of nano-devices. While the *bottom-up* techniques are yet to demonstrate their potential (although some substantial theoretical and experimental progress on this way has already been achieved, see [1]), a combination of *top-down* and *bottom-up* techniques – directed self-assembly – has already shown the potential of producing simple geometric patters, such as lines [2, 3].

Let us start by deriving the effective interaction potential between particles partially submerged in water. It has been shown [4] that surface tension forces are dominating for the micron-size particles, which resulted in the power law for particle interaction. For much smaller and larger scales which are of interest to us, van-der-Waals forces or gravity must be taken into account as well. This will form a surprising mathematical link between *cheerios effect*, where interface is deformed by surface tension and gravity, and the theory for self-assembly at nano-scales. We shall show that mathematically, the phenomena of particle attraction on millimeter and nano-meter scales are completely equivalent, in spite of very different physics. For the purpose of simplicity, we shall assume that the deviation of the surface level from the equilibrium is small, so the evolution of the interface is governed by *linear* equations. Notice that this does not assume that the interactions between the particles are linear in nature. Indeed, we shall show that the finite size of the particles and their relative spatial position play an important role in the interaction.

Particles embedded in the interface deform it, and gravity (in case of millimeter particles) or van der Waals forces (nm size particles) try to bring the surface back [5, 6, 7]. In both cases, the surface is goverened by the Helmholtz equation

$$l_c^2 \Delta h - h = 0 \tag{1}$$

with capillary length l_c being several mm for the 'cheerios' case and 300 nm for 100 nm nano-particles. Equation (1) must be supplemented by boundary conditions at the boundary of each particle. We choose to specify contact angle of water-particle-air interface. Exact value of derivative of $h(x, y)$ with respect to the normal to the water/particle boundary is a nonlinear function of the water level, as the angle of the normal to a sphere relative to the horizontal plane at a given level changes when that level rises or sinks. We shall not try to attempt to incorporate this nonlinear boundary condition into our scheme here. Instead, we use linear approximation again and postulate that the derivative of the interface normal to the particle is specified. Since we are interested in small surface deviations from equilibrium and due to the linearity

of equation (1), we shall re-scale the value of the normal derivative of $h(x,y)$ at the boundary to be 1, as this derivative is assumed to be the same for all particles. This approximation is only valid if we posit that the equilibrium level of water is the same for all particles, and all particles are identical in size, as well as their wetting properties. Thus, we augment the equation (1) by the following boundary condition on the boundary of each disk D_k

$$\frac{\partial h}{\partial n}\left[(x,y)\in D_k\right]=1. \tag{2}$$

These physical considerations show that interaction potentials proportional to the Green's function for the Helmholtz operator plays a fundamental role in particle self-assembly across surprisingly many orders of magnitude. Thus, we shall consistently use the interaction potential derived from inverting the Helmholtz operator (Bessel functions, see below) in all of our numerical simulations.

2. The numerical scheme

The goal of this paper is to find a numerical solution to the following problem. We need to find interaction potential of N disks of radius R with their centers positioned at $\mathbf{r}=\mathbf{c}_i=(x_i,y_i)$, $i=1,\ldots,N$. In order to do that, we need to find the deformation of water surface $h(x,y)$ which is described by equation (1) with boundary conditions (2).

To use Green's function methods, let us add a set of δ-functions to the right-hand side of equation (1). We adjust the strength of these δ-function so it neutralizes the flux from the boundary. More precisely, we reformulate the problem (1-2) by positioning a set of δ-function at the center of each disk $\mathbf{c}_k$ to the right-hand side of (1):

$$l_c^2\Delta h-h=A\sum_{k=1}^{N}\delta\left(\mathbf{r}-\mathbf{c}_k\right)\ , \tag{3}$$

where R is the radius of the discs, $K_1(x)$ is the modified Bessel function of the second kind and A is given by

$$A=\frac{l_c}{K_1\left(R/l_c\right)}. \tag{4}$$

Since $K_0'(x)=K_1(x)$, the boundary condition (2) becomes

$$\frac{\partial h}{\partial n}\left[\mathbf{r}\in D_i\right]=AF_i(\mathbf{r}) \tag{5}$$

with

$$F_i(\mathbf{r})=\sum_{k\neq i}K_1\left(|\mathbf{r}-\mathbf{c}_k|\right)\frac{\left(\mathbf{r}-\mathbf{c}_k,\mathbf{n}(\mathbf{r})\right)}{|\mathbf{r}-\mathbf{c}_k|}\ , \tag{6}$$

where $\mathbf{n}(\mathbf{r})$ denotes the outward normal to the disk at the point $\mathbf{r}\in D_i$ and $(\mathbf{a},\mathbf{b})$ is the scalar product of vectors $\mathbf{a}$ and $\mathbf{b}$.

We seek a solution to the problem (3-5) using integral formulation. On the boundary of each disk, we set a continuum of point charges with density $\rho(\mathbf{r})$. For each disk i, the density of these charges $\rho(\mathbf{r})$ satisfies the following Fredholm integral equation of the first kind:

$$\sum_{k\neq i}\int_{\mathbf{r}'\in D_k}K_1\left(|\mathbf{r}-\mathbf{r}'|\right)\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r})\mathrm{d}\mathbf{r}'=F_i(\mathbf{r})\ , \tag{7}$$

with $F_i(\mathbf{r})$ given by (6).

Equation (7) can be solved by two methods: either direct discretization of (7) or using FFT (Fast Fourier Transform) methods. Both methods are roughly the same in both efficiency and accuracy, so we used two methods on a benchmark problem (two disk attraction) in order to be sure of the reliability of our code. All numerical results presented in this paper were obtained by the direct discretization method. The integral in (7) is discretized and the corresponding linear equation with full matix is inverted. If N disks are considered and K discretization points are used on each disk, we need to solve a linear equation with NK unknowns. Since the matrix is full and unstrctured, this will require $O((NK)^2)$ operations.

The resulting potential energy due to disk attraction is proportional to the elevation of the interface from its undisturbed value at the disk boundary. The potential energy for the set of disks with centers positioned at $\mathbf{c}_k$, $k=1\ldots N$ is thus

$$E[\mathbf{c}_1,\ldots,\mathbf{c}_N]=\sum_{k=1}^{N}\int_{|\mathbf{r}-\mathbf{c}_k|=R}h(\mathbf{r}(s_k))\mathrm{d}s_k\ , \tag{8}$$

where s_k denotes arclength parametrization of the boundary of k-th disk. The force on k-th disk is computed as minus the gradient of the energy (8) with respect to the position of k-th disk's center $\mathbf{c}_k$:

$$\mathbf{F}_k=-\frac{\partial E}{\partial\mathbf{c}_k}\ . \tag{9}$$

While it is possible to derive an analytic expression for the force (9) provided that the solution of (3-5) is known, we have discovered that it is more advantageous (and simple) to perform the differentiation in (9) numerically for the type of problems we are going to consider here.

Having finished the discussion of the algorithm, we now turn our attention to the results. We shall describe two problems. First, as a calibration problem, we shall compute the force of interaction between two disks and compare it with the theoretical estimates from the literature. Second, we shall investigate the

interaction between three particles and compare our results with the assumption of *geomteric screening* which has been used in many-particles simulations.

3. Two particle interaction

The problem of two disks which are attracted due to the effect of surface tension has been understood rather well. We shall not go into details here and will just refer the reader to the literature. In particular, it has been shown [5, 6] that two particles separated by a distance l have interaction potential proportional to $\exp(-l/l_c)$ in one dimension, and $K_0(l/l_c)$ in two dimensions ($K_0(x)$ being the modified Bessel function of the first kind). The force between the particles is then proportional to $K_1(l/l_c)$, and this result holds for both floating and partially submerged particles, although the coefficient in front of the Bessel function is strongly dependent on the physical properties, such as whether particles are floating or submerged, contact angle, particle geometry etc. Mathematically, these interaction potentials arise from inversion of Helmholtz operator in (1). In the analytical expressions cited above, the force was computed in the approximation that the disturbance created by a single disk is unaffected by the presence of the second disk. This is expected to be the case when disks are far apart, but of course it is interesting to know how this approximation compares with the results of full numerical solution. In our simulations, we have computed the force for the range of distances d separating the disks from $d = 2.2R$ (with R being disks' radius) to $d = 10R$. The results (not shown here for lack of space, see [8] for details) give an excellent agreement between predicted and computed force.

4. Geometric model of screening

Traditional model of particles' screening by capillary attraction [9, 10] incorporates geometric argument to find out the magnitude of the forces. The force $F_0(d)$ between any two unobstructed particles is dependent on the absolute value of the distance d only and is directed towards the center of the particles. Thus, the force acting on A due to interaction with B is simply

$$\mathbf{F}_{AB} = F_0\left(d_{AB}\right)\mathbf{n}_{AB},$$

where $\mathbf{n}_{AB}$ is a unit vector pointing from the center of A towards B. The force on the particle A due to interaction with C is less, as only a portion $\theta/(\theta+\phi)$ of this particle is visible. Thus,

$$\mathbf{F}_{AC} = \frac{\theta}{\theta+\phi}F_0\left(d_{AC}\right)\mathbf{n}_{AC}. \qquad (10)$$

The total force acting on the particle A is then just $\mathbf{F}_A = \mathbf{F}_{AB} + \mathbf{F}_{AC}$. One can prove that for this geometric screening model, the force is not potential by showing that the work over a specified closed contour is not zero [8]. This observation is important, since we expect that the force between arbitrary many particles should be potential, as it comes from minimization of surface energy of the interface. We will now show that the geometric model of screening does not adequately describe the magnitude of forces between particles in a specific three-particle configuration.

5. Numerical results for interaction of three particles and comparison with geometric screening models

To study the validity of geometrical screening quantitatively, we performed a numerical study of the system illustrated on Fig. 1. The x direction is horizontal and y direction is vertical. Disks B and C are positioned on the horizontal line at the distance D. Disk A is also positioned at the distance D from disk A, but the line connecting the centers of A and B forms angle α with respect to horizontal. The distance between the disks was chosen to be $D = 2.5R$, where R is disk's radius. When $\alpha = \pi/2$, there is no screening, and when $\alpha = 0$, there should be no force exerted on A by C according to the geometrical screening ansatz. We have chosen to re-scale all the forces so they will be equal to 1 when $\alpha = \pi/2$. The results of the simulations are shown on Fig. 2. We have only shown the forces and not the interaction potential since geometric screening breaks the potential nature of the interaction force as we discussed above. The forces from full numerical simulation are marked with stars. The forces calculated from geometric screening are shown with crosses. For comparison, we have also presented the forces which result from taking a simple vector sum of forces between individual particles (marked with circles). The results summarized on Fig. 2 clearly show that both the simple vector sum and geometric screening severely under-estimate the magnitude of the forces acting on particles in x direction, while providing fair comparison for the y direc-

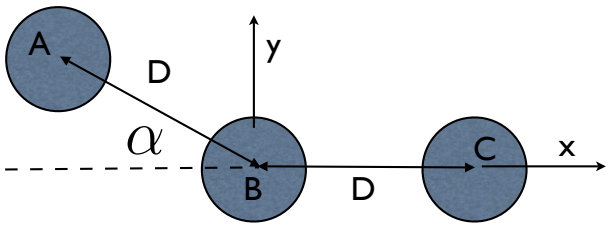

Figure 1: Explanation of notation used in the numerical study of screening of forces between three disks. The distances between centers of the disks A-B and B-C are equal to D, and the line A-B is rotated with respect to horizontal by the angle α.

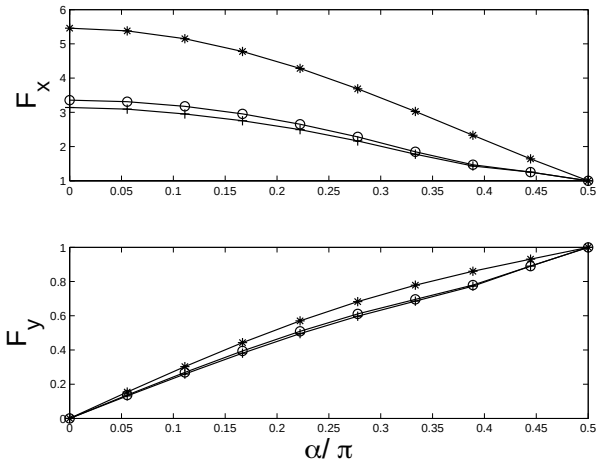

Figure 2: A comparison of attractive forces between three disks computed from numerics ($*$) and theoretically computed interactions using a sum of individual forces of attraction between particles. The simple vector sum of dual interactions is marked with circles and the geometrically screened sum is denoted with crosses.

tion. We observe an *amplification* of forces for small α, when the screening should have been the strongest. In particular, our simulation shows that for particles on a line ($\alpha = 0$) there is a strong interactive effects even from the particles which are not visible.

6. Conclusions

We have found interaction potential between partially wetting particles which are attracted by the force of surface tension. Our results were obtained in the approximation of small deviation of water level from its equilibrium value, so the equation for surface elevation $h(x, y)$ (1) is linear. Nonlinearity in the problem considered here comes from the domain where the problem is solved, namely, the plane without several disks. The corresponding forces on the particles are computed and compared with several established model of multiparticle interactions. Our studies show that models of screening for Helmholtz interactions based on geometric visibility criteria need correction. We shall emphasize that we have only studied three particle interactions in the system with interface elevation described by Helmholtz equation. Geometric screening may still be valid (perhaps in some averaged sense) when particle motion is due to several competing physical reasons or, alternatively, a when great number of particles is present, as was the case in [9, 10]. Constructing a valid screening model derived from the first principles is a difficult problem which must be addressed in the future.

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